

# G2 *Ab Initio* Calculations on Three-Membered Rings: Role of Hydrogen Atoms

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**ABSTRACT:** G2 *ab initio* calculations on all ABX three-membered rings (TMRs) that can be derived from cyclopropane by systematic substitution of the  $-\text{CH}_2$  groups by  $-\text{NH}$  or  $-\text{O}$  groups have been performed. Our results show that the decrease in the A—B bond length as the electronegativity of X increases is significantly larger than that found for the corresponding acyclic analogs. In general, a systematic substitution of the  $-\text{CH}_2$  groups of cyclopropane by  $-\text{NH}$  or  $-\text{O}$  groups implies significant geometric changes that are not reflected in a parallel change of the corresponding conventional ring strain energy (CRSE). When the electronegativity of the groups forming the TMR increases the effect on the CRSE of the system is small, although the charge delocalization inside the ring decreases. The near constancy of the CRSE along the series can be explained in terms of the charge redistribution of the system where the  $-\text{CH}_2$  groups play a crucial role. There are, however, significant changes in the hydrogenation energies of the TMR investigated; our results show that, when in an ABX three-membered ring, the electronegativity of X increases the hydrogenation energy of A—B bond decreases and vice versa. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 1072–1086, 1998

**Keywords:** three-membered rings; G2 theory; ring-strain; hydrogenation energies

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## Introduction

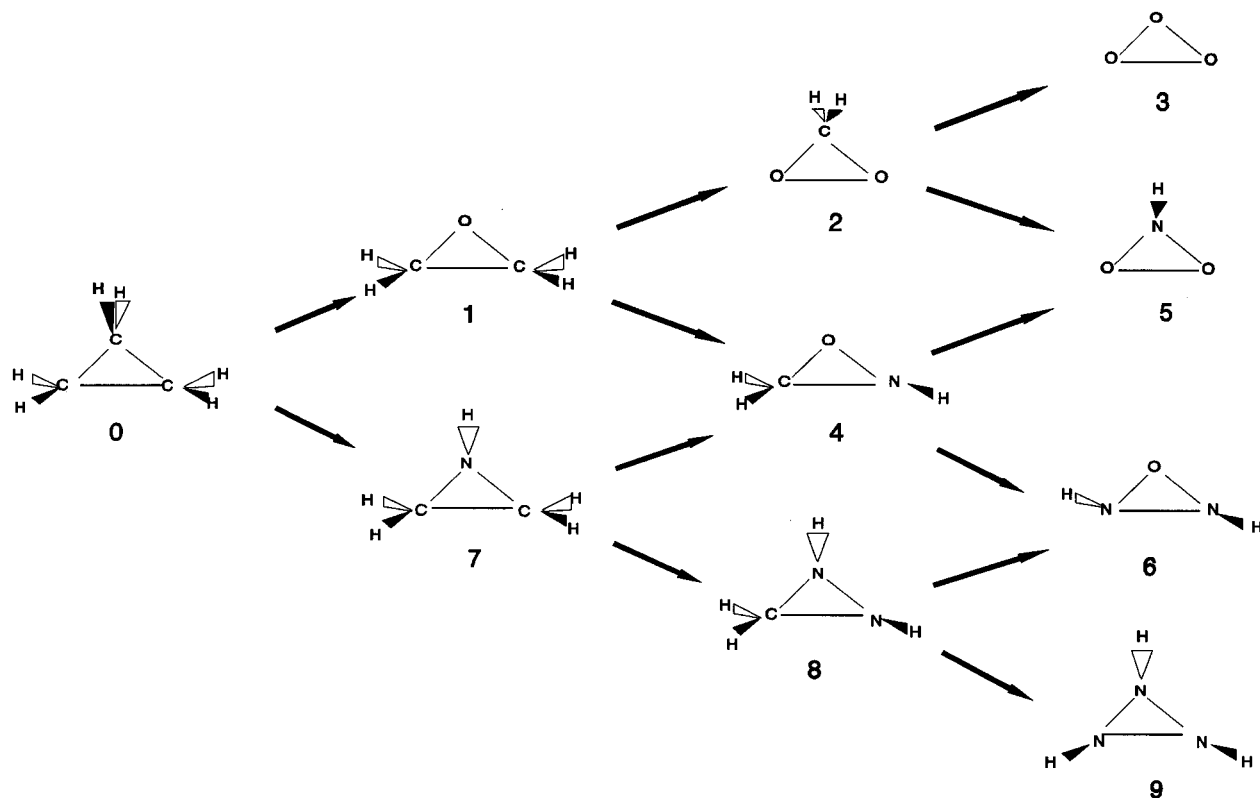
The study of the structure and reactivity of three-membered rings (TMRs) has been a topic of considerable interest for chemists from both the experimental<sup>1–6</sup> and theoretical<sup>7–27</sup> points of view. One of the most outstanding features of TMRs is their anomalous ring strain. Pertaining to geometrical criteria, TMRs should represent the group of molecules with highest ring strain, nevertheless, their strain is lower than expected.<sup>28–32</sup> In this respect it is well established that cyclopropane is only 1.0 kcal/mol more strained than cyclobutane. In the case of O or N containing TMR, Zhao and Gimarc<sup>31,32</sup> have theoretically predicted N<sub>3</sub> and O<sub>3</sub> to be *less* strained than N<sub>4</sub> and O<sub>4</sub> by 6.9 and 2.9 kcal/mol, respectively.

Different effects have been proposed<sup>33–40</sup> to explain these results either by considering the four-membered rings as being anomalously destabilized or the TMR as being additionally stabilized. One of the most appealing theories states that

cyclopropane is stabilized by a delocalization of the  $\sigma$ -electrons inside the ring ( $\sigma$ -aromaticity).<sup>33–36</sup> Although this theory would explain several properties of cyclopropane it has recently been the subject of some controversy in the literature.<sup>39,40</sup> A quite complete compilation and discussion of the different models proposed in the literature to rationalize the properties of three-membered rings and, in particular, their ring strain energies, can be found in ref. 41.

Most studies concerning ring strain in TMRs have focused on comparison of the properties of TMRs with analogous rings of different size.<sup>31,32,36,38,40</sup> In this study, we envisage a different approach: we have selected all of the saturated TMRs that can be formed by systematic substitution of the CH<sub>2</sub> groups of cyclopropane by —O or —NH groups (see Fig. 1) to analyze how the different properties of the molecules, ring strain, etc., change when changing the atoms of the ring.

Most of the TMRs considered in this work (cyclopropane, 0; oxirane, 1; dioxirane, 2; oxaziridine, 4; oxadiaziridine, 6; aziridine, 7; diaziridine, 8; and triaziridine, 9) are known to be experimen-



**FIGURE 1.** Three-membered rings included in this study. Ascending arrows indicate substitution of —CH<sub>2</sub> group by an —O. Descending arrows indicate substitution of —CH<sub>2</sub> group by an —NH.

tally stable and present a rich chemistry or are the active parts of larger systems.<sup>1–5</sup> Since the 1973 study by Lathan et al.,<sup>7</sup> in which the structures of all TMRs containing C, N, and O were calculated using *ab initio* methods, many of these compounds have been recalculated at higher levels of accuracy.<sup>14–27,32,36–41</sup> However, there is a lack of systematic investigation at high *ab initio* levels, including all TMRs presented in Figure 1, which permits rationalization of their behavior.

As mentioned earlier, the set of molecules selected will permit investigation of changes in properties of TMRs as the  $-\text{CH}_2$  groups of cyclopropane are substituted by O ( $0 \rightarrow 1 \rightarrow 2 \rightarrow 3$ , represented by ascending arrows in Fig. 1), or by  $-\text{NH}$  ( $0 \rightarrow 7 \rightarrow 8 \rightarrow 9$ , represented by descending arrows in Fig. 1). Molecules in which both O and  $-\text{NH}$  groups form part of the ring lie between these two series. Ascending and descending arrows keep their meaning throughout the entire diagram.

The systematic substitution of the  $-\text{CH}_2$  groups by more electronegative substituents will put in evidence general trends that confirm the important role of the relative strength of the C—H bonds when discussing the stability of strained systems, pointed out previously in the literature by Schleyer,<sup>13</sup> Hamilton and Palke,<sup>20</sup> and more recently by Johnson and Borden.<sup>27</sup> We will show that this implies an important stabilizing role of the  $-\text{CH}_2$  hydrogens, which was also observed by Wiberg et al.<sup>42</sup> for the particular case of carbocations and carbanions.

## Computational Details

The geometries of all the systems included in Table II have been fully optimized at HF level and refined at the MP2 level<sup>43</sup> using the 6-31G\* basis set.<sup>45</sup> All electrons have been included in the MP2 treatment. Frequencies have been evaluated at HF/6-31G\*. From these calculations we have verified that all structures presented in Figure 1 are actual minima of the potential energy surfaces. Zero-point energies (ZPE) have been corrected using standard scaling factors.<sup>46</sup> For the open-chain structures the most stable conformation has been taken from the literature when available,<sup>31,32,47–51</sup> otherwise, all possible conformers have been considered in the geometry optimization and frequency calculations. Hereafter, for the sake of conciseness, all reported data for the open-chain

structures will refer to the most stable conformation. The geometries of these species are given as Supplementary Material.

To obtain reliable heats of formation and atomization energies, the total energies for the most stable conformer of the compounds included in Table II were obtained at the G2 level of theory.<sup>52</sup> G2 theory has been specially designed to yield heats of formation, atomization energies, and other thermodynamic magnitudes within an average error of 1.2 kcal/mol. Calculations were restricted to the G2 (MP2)<sup>53</sup> level only when large open-chain compounds were studied (structures 40–44).

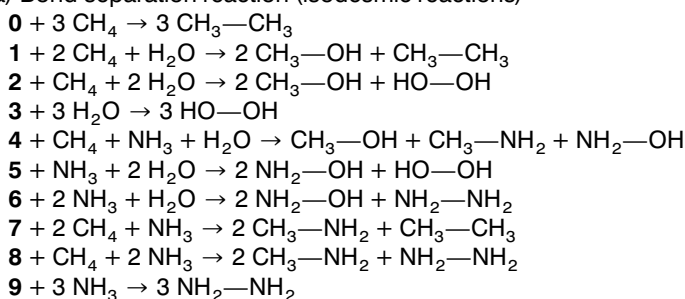
The topological analysis of the electronic charge density,  $\rho(\mathbf{r})$  and its Laplacian,  $\nabla^2\rho(\mathbf{r})$ , is a powerful tool to describe the characteristics of bonds and interactions.<sup>54–56</sup> In particular, the critical points of  $\rho(\mathbf{r})$ , which present two negative curvatures and one positive curvature, identify the bonds in the molecule and will be denoted hereafter as bond critical points (bcp). The lines of maximum charge density linking the nuclei are called bond paths, and the angles between them bond path angles. The critical points with one negative and two positive curvatures are associated with the existence of a ring structure and will be denoted as ring critical points (rcp). The values of  $\rho(\mathbf{r})$  and  $\nabla^2\rho(\mathbf{r})$  at these points provide quantitative information on the strength and nature of the bonding and the characteristics of the ring. The Laplacian of the electronic charge density,  $\nabla^2\rho(\mathbf{r})$ , identifies<sup>56</sup> regions of space wherein  $\rho(\mathbf{r})$  is locally concentrated [ $\nabla^2\rho(\mathbf{r}) < 0$ ] or depleted [ $\nabla^2\rho(\mathbf{r}) > 0$ ]. In general, negative values of  $\nabla^2\rho(\mathbf{r})$  are typical of covalent interactions, whereas interactions between closed-shell systems are characterized by positive values of  $\nabla^2\rho(\mathbf{r})$ . There are, however, some significant exceptions to this general behavior, particularly when very electronegative atoms are involved in the bond. A more reliable index would be the energy density,<sup>57</sup>  $H(\mathbf{r})$ , because negative values of this parameter at the bcp are associated with stabilizing charge concentrations within the bonding region. In this respect, it should be mentioned that the atoms-in-molecules theory of Bader has been used extensively by Cremer and Gauss<sup>36</sup> and Cremer and Kraka<sup>34,35</sup> to discuss strain effects in cyclic compounds.

We will use the definition of conventional ring strain energy (CRSE) of a molecule as the negative of the energy change associated with the homodesmotic reactions<sup>58</sup> as summarized in Table I,

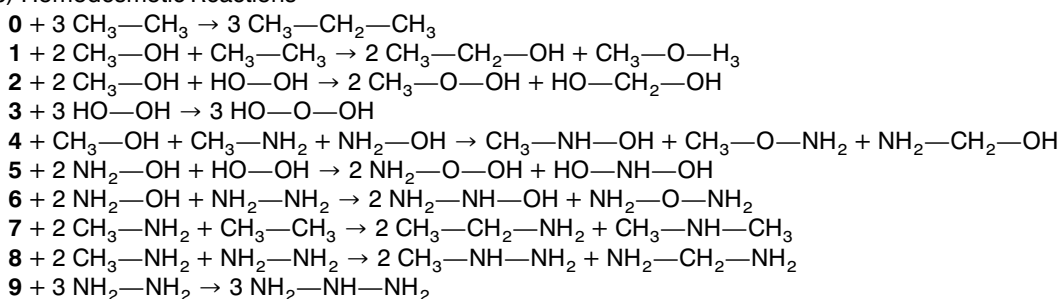
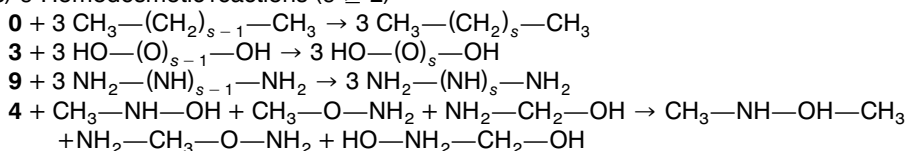
TABLE I.

Definition of Isodesmic, Homodesmotic, and s-Homodesmotic Reactions Used in This Study.

## (a) Bond separation reaction (isodesmic reactions)



## (b) Homodesmotic Reactions

(c) s-Homodesmotic reactions ( $s \geq 2$ )

which involve the set of open-chain molecules included in Table II. The CRSEs evaluated in this way usually agree with the experimental values and greatly improve the agreement reached when isodesmic reactions (also defined in Table I) are used.

All *ab initio* calculations have been performed using the Gaussian-94<sup>59</sup> program package. The electron density analysis has been carried out using the AIMPAC<sup>60</sup> series of programs.

## Results and Discussion

The G2 energies of the most stable conformers of the compounds included in this study are summarized in Table II. The atomization enthalpies, formation enthalpies, bond separation energies (BSE), hydrogenation energies (HE), and CRSE of the TMR included in this study are given in Table



III, whereas the geometrical parameters are included in Table IV (bond lengths) and Table V (ring angles).

## GEOMETRIES

It can be reasonably expected that the main properties of the TMR are due to their unusual geometries, which force the hybridization of the atoms forming the ring to be quite different from that of the open-chain structures. This should be reflected in many of their properties and primarily in their geometries. For this reason we begin our discussion by analyzing: (a) how distances and angles are modified when the atoms forming the rings change; and (b) how the bond distances differ from those found for the open-chain homolog structures.

To perform such an analysis in a systematic way, we summarize, in Table IV, the properties of the different bonds of the ring, which have been

TABLE II. G2 Energies (a.u.) at 0 K for all Compounds Included in this Study.<sup>a</sup> [Values in Parentheses Correspond to G2 (MP2) Values, and Values in Brackets Correspond to CBS-APNO Values.]

0	Cyclopropane	-117.63109	13	CH <sub>3</sub> —CH <sub>3</sub>	-79.63090 <sup>a</sup>	26	CH <sub>3</sub> —O—NH <sub>2</sub>	-170.74580	39	HO—(O) <sub>2</sub> —OH	-301.48163 (-301.47256)
1	Oxirane	-153.53286	14	CH <sub>3</sub> —NH <sub>2</sub>	-95.66691 <sup>a</sup>	27	CH <sub>3</sub> —O—OH	-190.58241	40	CH <sub>3</sub> —NH—O—CH <sub>3</sub>	-209.96655
2	Dioxirane	-189.37215 [-189.58583]	15	CH <sub>3</sub> —OH	-115.53489 <sup>a</sup>	28	NH <sub>2</sub> —CH <sub>2</sub> —NH <sub>2</sub>	-150.93767	41	NH <sub>2</sub> —CH <sub>2</sub> —O—NH <sub>2</sub>	-245.89342
3	Trioxirane	-225.12272 (-225.11683) [-225.361988]	16	NH <sub>2</sub> —NH <sub>2</sub>	-111.68045 <sup>a</sup>	29	NH <sub>2</sub> —CH <sub>2</sub> —OH	-170.81111	42	HO—CH <sub>2</sub> —NH—OH	-226.02219
4	Oxaziridine	-169.53372	17	NH <sub>2</sub> —OH	-131.53331	30	NH <sub>2</sub> —NH—NH <sub>2</sub>	-166.91936	43	NH <sub>2</sub> —(NH) <sub>3</sub> —NH <sub>2</sub>	(-277.39341)
5	Dioxaziridine	-205.32839	18	HO—OH	-151.36578 <sup>a</sup>	31	NH <sub>2</sub> —NH—OH	-186.77881	44	HO—(O) <sub>3</sub> —OH H <sub>2</sub>	(-376.52748)
6	Oxadiaziridine	-185.51435	19	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>3</sub>	-118.85582 <sup>b</sup>	32	NH <sub>2</sub> —O—NH <sub>2</sub>	-186.74698	45		-116.95774
7	Aziridine	-133.66422	20	CH <sub>3</sub> —CH <sub>2</sub> —NH <sub>2</sub>	-134.89454	33	NH <sub>2</sub> —O—OH	-206.58877	46		-152.86716
8	Diaziridine	-149.68274	21	CH <sub>3</sub> —CH <sub>2</sub> —OH	-154.76446 <sup>c</sup>	34	HO—CH <sub>2</sub> —OH	-190.68361			-1.16636 <sup>a</sup>
9	Triaziridine	-165.67951 (-165.67628)	22	CH <sub>3</sub> —NH—CH <sub>3</sub>	-134.88280 <sup>c</sup>	35	HO—NH—OH	-206.62786			-0.50000 <sup>a</sup> [-0.49995]
10	CH <sub>4</sub>	-40.401088 <sup>a</sup>	23	CH <sub>3</sub> —NH—NH <sub>2</sub>	-150.89995	36	HO—O—OH	-226.42438			-37.78432 <sup>a</sup> [-37.84208]
11	NH <sub>3</sub>	-56.45865 <sup>a</sup>	24	CH <sub>3</sub> —NH—OH	-170.74837	37	CH <sub>3</sub> —(CH <sub>2</sub> ) <sub>2</sub> —CH <sub>3</sub>	-158.08117 <sup>d</sup>			-54.51798 <sup>a</sup>
12	H <sub>2</sub> O	-76.33205 <sup>a</sup>	25	CH <sub>3</sub> —O—CH <sub>3</sub>	-154.74664 <sup>c</sup>	38	NH <sub>2</sub> —(NH) <sub>2</sub> —NH <sub>2</sub>	-222.15955 (-222.15406)			-74.98203 <sup>a</sup> [-37.84208]

<sup>a</sup> Value taken from ref. 51. <sup>b</sup> Value taken from ref. 48. <sup>c</sup> Value taken from ref. 47. <sup>d</sup> Value taken from ref. 49.

**TABLE III.**  
**Enthalpies and Energies.**

Compound	$\Delta H_a$	$\Delta H_f^{\text{at}}$	$\Delta H_f^{\text{iso}}$	BSE	HE <sup>a</sup>	CRSE
<b>0</b>	802.0	17.6	17.0 (16.9) <sup>a</sup>	−18.2 (−18.1) <sup>b</sup>	−36.6 (−37.7) <sup>b</sup> ( <b>19</b> ) <sup>c</sup>	27.4 / 28.2 (27.5) <sup>d</sup>
<b>1</b>	616.3	−10.8	−9.7 (−9.6) <sup>a</sup>	−8.8 (−8.9) <sup>b</sup>	−40.9 (−42.3) <sup>b</sup> ( <b>21</b> ) −29.8 (−30.1) <sup>b</sup> ( <b>25</b> )	26.4 (27.2) <sup>d</sup>
<b>2</b>	391.4 [389.4]	−0.2 [1.3]	2.7	+7.3	−91.1 ( <b>34</b> )	25.6
<b>3</b>	110.8 [111.8]	66.2 [65.2]	64.6	+13.5	−84.9 ( <b>36</b> )	33.3 / 30.8 / 30.1 (23.8) <sup>e</sup>
<b>4</b>	470.3	26.1		+0.1	−69.7 ( <b>29</b> ) −30.3 ( <b>24</b> ) −28.7 ( <b>26</b> )	22.9 / 27.1
<b>5</b>	217.3	64.8		+11.8	−83.5 ( <b>35</b> ) −59.0 ( <b>33</b> )	28.0
<b>6</b>	311.5	75.8		+10.4	−61.6 ( <b>31</b> ) −41.6 ( <b>32</b> )	27.1
<b>7</b>	676.2	34.5		−12.6 (−16.3) <sup>b</sup>	−40.1 (−42.0) <sup>b</sup> ( <b>20</b> ) −32.8 (−34.6) <sup>b</sup> ( <b>22</b> )	27.0 (27.1) <sup>d</sup>
<b>8</b>	541.2	60.4		−2.1	−55.6 ( <b>28</b> ) −31.9 ( <b>23</b> )	25.5
<b>9</b>	392.6	99.9	97.6	+8.9	−45.0 ( <b>30</b> )	23.4 / 24.8 / 26.2 (28.8) <sup>f</sup>

$\Delta H_a$ , Atomization Enthalpies at 0 K;  $\Delta H_f^{\text{at}}$ , Formation Enthalpies at 0 K from the atomization reaction;  $\Delta H_f^{\text{iso}}$ , Formation Enthalpies at 0 K from the isodesmotic reaction; (BSE), bond separation energies; HE, Hydrogen energies; CRSE, conventional ring strain energies, from the homodesmotic reactions defined in Table I. When more than one value is given, the second and third value correspond to the *s*-homodesmotic reactions of orders 2 and 3, respectively. All quantities are given in kcal/mol and have been calculated at the G2 level except the *s*-homodesmotic cases of order 3, which have been calculated at G2 (MP2) level and numbers within brackets, which have been calculated at CBS-APNO level. Available experimental values are given between parentheses.

<sup>a</sup> Values taken from ref. 29a. <sup>b</sup> Values calculated from the corresponding experimental heats of formation taken from ref. 29a. <sup>c</sup> Bold values designate the products of the hydrogenation reactions. <sup>d</sup> Experimental value taken from ref. 29b. <sup>e</sup> Theoretic value taken from ref. 32 for the *s*-homodesmotic reaction of order 3 at the MP2/6-31G\* level. <sup>f</sup> Theoretical value taken from ref. 31 for the *s*-homodesmotic reaction of order 4 at the MP2/6-31G\*\* level.

grouped according to their nature. For each bond, X represents the third atom of the TMR. For comparison we have also included in this table the bond lengths of the corresponding open-chain homologs (**13** to **36**).

It can be observed that all bond distances become shorter as the electronegativity of X increases, this effect being twice as large for TMRs than for open-chain forms. An electronegative substituent X withdraws charge from the two atoms to which it is attached, and enhances their electronegativities. As a consequence, their *s* character increases and the bond between them becomes shorter. These changes are nicely visualized by means of a natural bond orbital (NBO)<sup>61</sup> analysis. As illustrated in Table VI, when one or the two —CH<sub>2</sub> groups in cyclopropane **0** are replaced by —O to yield species **1** or **2**, respectively, the *s* character of the remaining carbon atoms increases. This is consistent with the widening of the HCH angle of the —CH<sub>2</sub> groups (see Table VI) and with the fact that the CH<sub>2</sub> hydrogens become more acidic. Accordingly, the charge density at the C—C

bcp also increases and both  $\nabla^2\rho$  and  $H(\mathbf{r})$  become more negative (see Table IV). Similar effects, although smaller, are found when the —CH<sub>2</sub> groups are replaced by —NH groups to yield species **7** and **8**. The same arguments can be invoked to explain the shortening of the HN—NH bonds when going from **8** to **9** and **6**. In these cases, the degree of pyramidalization of the —NH groups increases upon substitution, the NH hydrogens become more acidic, and the nitrogen atoms less basic.<sup>23</sup> These obvious effects will be of paramount importance when discussing the strain and properties of TMRs.

A comparison of the bond distances of open-chain and ring structures could give an idea of how the bonds are reinforced/weakened upon ring formation. For instance, in cyclopropane CC bonds are known to be shorter than in open-chain alkanes.<sup>30,34–41</sup> This difference in the CC distance is bigger when there exists a heteroatom in the ring (as in **1** or **7**) for the reasons indicated earlier. Nevertheless, there are many cases (see Table IV) in which the opposite trend is found. For instance,

N—N distances are always larger in TMRs than in the corresponding open-chain systems. Two main factors seem to be responsible for these effects: (a) the tendency to keep ring angles as close to 60° as possible to minimize the angular strain energy (ASE); and (b) the role of the H atoms attached to C atoms being the most polarizable part of the rings.

Consider, once more, the changes when a CH<sub>2</sub> group of cyclopropane is replaced by —O. Because C—O bonds are intrinsically much shorter than C—C linkages (XY bond distances follow the sequence CC > OO > CN > NO > NN > CO), the replacement would imply large changes in the angles forming the ring, increasing the ASE. The only way to avoid this destabilization is by shortening the CC bond and enlarging the CO bonds. This is what actually happens. Both bond lengths become very similar in **1** (1.463 and 1.437 Å, re-

spectively, when they normally differ by 0.1 Å; see Table IV) leading to geometrical ring angles close to 60° (Table V). Similar trends are observed when the bond path lengths and bond path angles are considered instead of the geometrical ones (see Tables IV and V). However, these geometrical changes require a large charge redistribution, because the shortening of the bonds necessarily implies an increment of their bonding charge density. This charge can be easily obtained from the —CH<sub>2</sub> groups and, to a much lesser degree, from the —NH groups, whereas no charge can be withdrawn from an —O group. Hence, when a second —CH<sub>2</sub> group is substituted by —O (going from **1** to **2**), attending to the ASE criteria, a lengthening of the C—O bond and a shortening of the OO bond should occur. However, what is actually found in **2** is a shortening of the C—O bonds because there is no way to accumulate charge into

TABLE IV.  
Characteristics of Bonds in TMR.

Bond	X <sup>a</sup>	Comp.	R	ρ	∇ <sub>ρ</sub> <sup>2</sup>	H <sub>R</sub>	ε	R <sup>b</sup>
H <sub>2</sub> C—CH <sub>2</sub>	CH <sub>2</sub> NH O	<b>0</b>	1.502 (1.509)	0.240	−0.440	−0.204	0.490	1.524 ( <b>13</b> )
		<b>7</b>	1.479 (1.492)	0.251	−0.513	−0.223	0.357	1.524 ( <b>19</b> )
		<b>1</b>	1.463 (1.480)	0.260	−0.574	−0.238	0.266	1.526 ( <b>20</b> )
								1.512 ( <b>21</b> )
H <sub>2</sub> C—NH	CH <sub>2</sub> NH O	<b>7</b>	1.472 (1.476)	0.254	−0.519	−0.270	0.455	1.464 ( <b>14</b> )
		<b>8</b>	1.448 (1.456)	0.269	−0.652	−0.306	0.274	1.464 ( <b>20</b> ) 1.456 ( <b>22</b> )
		<b>4</b>	1.438 (1.449)	0.276	−0.735	−0.327	0.179	1.459 ( <b>28</b> ) 1.456 ( <b>23</b> )
								1.440 ( <b>29</b> ) 1.454 ( <b>24</b> )
H <sub>2</sub> C—O	CH <sub>2</sub> NH O	<b>1</b>	1.437 (1.439)	0.248	−0.481	−0.326	0.684	1.423 ( <b>15</b> )
		<b>4</b>	1.406 (1.411)	0.265	−0.504	−0.385	0.286	1.426 ( <b>21</b> ) 1.420 ( <b>25</b> )
		<b>2</b>	1.397 (1.404)	0.271	−0.542	−0.408	0.140	1.431 ( <b>29</b> ) 1.422 ( <b>26</b> )
								1.408 ( <b>34</b> ) 1.420 ( <b>27</b> )
HN—NH	CH <sub>2</sub> NH O	<b>8</b>	1.506 (1.508)	0.251	−0.166	−0.212	0.454	1.438 ( <b>16</b> )
		<b>9</b>	1.470 (1.477)	0.274	−0.305	−0.252	0.169	1.431 ( <b>23</b> )
		<b>6</b>	1.454 (1.462)	0.287	−0.392	−0.269	0.070	1.426 ( <b>30</b> )
								1.408 ( <b>31</b> )
HN—O	CH <sub>2</sub> NH O	<b>4</b>	1.512 (1.514)	0.235	0.094	−0.178	0.587	1.452 ( <b>17</b> )
		<b>6</b>	1.467 (1.472)	0.262	−0.073	−0.223	0.140	1.431 ( <b>24</b> ) 1.448 ( <b>26</b> )
		<b>5</b>	1.449 (1.456)	0.276	−0.169	−0.247	0.034	1.464 ( <b>31</b> ) 1.436 ( <b>32</b> )
								1.427 ( <b>35</b> ) 1.381 ( <b>31</b> )
O—O	CH <sub>2</sub> NH O	<b>2</b>	1.529 (1.531)	0.220	0.374	−0.143	0.717	1.469 ( <b>18</b> )
		<b>5</b>	1.488 (1.492)	0.242	0.231	−0.180	0.088	1.470 ( <b>27</b> )
		<b>3</b>	1.476 (1.482)	0.251	0.166	−0.193	0.053	1.506 ( <b>33</b> )
								1.441 ( <b>36</b> )

Bond distances (*R* in Å, corresponding bond path lengths are given in parentheses), charge density (*ρ*, in a.u./e<sup>3</sup>), Laplacian of the charge density (∇<sub>ρ</sub><sup>2</sup>, in a.u./e<sup>5</sup>), energy density (*H<sub>R</sub>*, in a.u./e<sup>5</sup>), and ellipticity (*ε*) at the corresponding bond critical point.  
<sup>a</sup> X refers to the third group forming the ring. <sup>b</sup> Distances corresponding to the open forms for the same bond and the same substituent heteroatom. Numbers in parentheses identify the compound from which the corresponding distance has been taken. In heteronuclear bonds, the first (second) value corresponds to the substituent attached to the less (more) electronegative atom of the bond. The first value of each group corresponds to the cases in which no substituent exists (compounds **13** to **18**).

**TABLE V.**  
**Characteristics of Rings in TMR.**

Compound		$\alpha$	$\beta$	$\rho$	$\nabla^2\rho$
0	C	60.0	76.7	0.199	0.090
1	C	59.4	70.8	0.212	0.282
	O	61.1	74.2		
2	C	66.4	73.1	0.205	0.571
	O	56.8	65.5		
3	O	60.0	78.4	0.176	0.776
4	C	64.2	74.0	0.210	0.411
	N	56.9	66.5		
5	O	58.9	72.4	0.195	0.665
	N	61.8	75.4		
6	O	59.1	77.0	0.206	0.522
	N	60.3	74.8		
7	O	59.4	78.2	0.208	0.174
	C	59.9	75.6		
8	N	60.3	75.1	0.213	0.273
	C	62.9	76.0		
9	N	58.6	73.0	0.212	0.385
	N	60.0	76.4		

Ring angle ( $\alpha$ , in degrees), bond path angle ( $\beta$ , in degrees), charge density ( $\rho$ , in a.u./e<sup>3</sup>), and Laplacian of the charge density ( $\nabla^2\rho$ , in a.u./e<sup>5</sup>) at the ring critical point.

the O—O bond, yet it is possible to do so into the C—O linkages, by polarizing the —CH<sub>2</sub> group. The overall positive charge of the —CH<sub>2</sub> groups increases significantly in a consistent manner as the number of electronegative groups within the ring increases (see Table VI where the net charges of the —CH<sub>2</sub> groups of 0, 1, and 2 are compared).

Finally, when the last CH<sub>2</sub> group is substituted by O (going from 2 to 3) the ASE criterion does not apply any longer, because the angles are equal to

60° for symmetry reasons. In this case, there are no CH<sub>2</sub> groups from which charge can be easily withdrawn and, consequently, all OO bonds are longer than in the open-chain form, just the opposite of what happened in cyclopropane 0.

Substitution of CH<sub>2</sub> by NH produces similar effects. For instance, the C—C and the C—N bond lengths of 7 are again rather similar, while a shortening of the C—N linkages takes place when going to species 8. Similarly, because the —NH groups are not very polarizable and charge cannot easily be withdrawn from them, species 9 has bond distances larger than the corresponding open-chain homolog (30).

### RING STRAIN AND ENERGETICS

There is no unique way of measuring the energy involved in the opening of the ring. The simplest reaction that can be used for this purpose is the hydrogenation reaction:



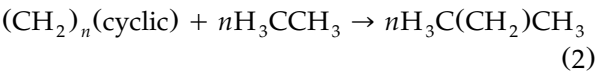
which is an isogyric process where the number of electron pairs at each side of the reaction remains unchanged. The set of bond-separation isodesmic reactions defined in Table I represents another alternative that keeps constant the nature and number of the bonds. The third alternative is the homodesmotic processes used to define the CRSE where, in addition to the nature and number of the bonds, the valence environment around each atom is also kept constant. These latter reactions, proposed by George et al.<sup>58</sup> as a way to evaluate the

**TABLE VI.**  
**Natural Electron Configuration (*s* and *p*) of Heteroatoms Forming Different Three-Membered Rings, Total Atomic Charge (*q*) of the CH<sub>2</sub>, NH, and O Groups, HCH Bond Angle (degrees), and CH and NH Distances (Å).**

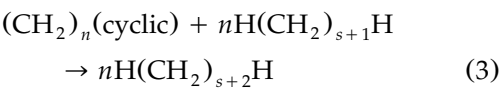
Compound	CH <sub>2</sub>					NH				O		
	<i>s</i>	<i>p</i>	<i>q</i>	HCH	<i>R</i> (CH)	<i>s</i>	<i>p</i>	<i>q</i>	<i>R</i> (NH)	<i>s</i>	<i>p</i>	<i>q</i>
0	1.03	3.40	0	114.2	1.084	—	—	—	—	—	—	—
1	1.05	3.05	+0.265	115.5	1.087	—	—	—	—	1.72	4.74	−0.532
2	1.06	2.70	+0.561	116.5	1.090	—	—	—	—	1.79	4.42	−0.280
3	—	—	—	—	—	—	—	—	—	1.87	4.06	0
4	1.05	2.87	+0.425	115.7	1.087	1.56	3.75	−0.018	1.028	1.76	4.57	−0.407
5	—	—	—	—	—	1.62	3.39	+0.281	1.035	1.83	4.23	−0.140
6	—	—	—	—	—	1.59	3.57	+0.138	1.030	1.81	4.39	−0.276
7	1.04	3.22	+0.142	114.7	1.087	1.47	4.14	−0.283	1.020	—	—	—
8	1.04	3.04	+0.294	114.9	1.087	1.53	3.93	−0.146	1.023	—	—	—
9	—	—	—	—	—	1.56	3.74	0	1.026	—	—	—



ring strain in cycloalkanes, can be written as:



This concept has been generalized by Zhao and Gimarc,<sup>31,32</sup> by defining the *s*-homodesmotic reactions:



For *s* = 0, the isodesmic reaction is obtained, for *s* = 1 the homodesmotic, and for *s* = 2 the hyperhomodesmotic. It was also shown<sup>31,32</sup> that a poor estimation of the CRSE was obtained for *s* = 0 (isodesmic reaction), whereas, for *s* = 1 (homodesmotic reactions), there was significant improvement, especially when calculations were performed at the MP2/6-31G\* level,<sup>31,32</sup> even though the calculated CRSEs still differ from the experimental ones. In the same studies, a convergence of the predicted CRSEs for compounds **3** and **9** was obtained for values of *s* = 2 and *s* = 3, respectively.

HYDROGENATION ENERGIES

The results in Table III show that the hydrogenation energies vary within wide limits (27.5–91.1 kcal/mol). More importantly, they depend on the charge deficiency of the bond that undergoes the hydrogenation. This charge deficiency is clearly reflected in the Laplacian of the charge density as well as in the energy density, *H*(**r**) at the bcp. Electron-deficient bonds greatly stabilize upon hydrogenation because it is possible withdraw charge from the new X—H bonds and, consequently, large values of hydrogenation energies are obtained. Accordingly, there exists a fairly good linear correlation between the calculated hydrogenation energies and the value of ∇<sup>2</sup>*ρ* at the bcp of the linkage involved in the reaction (see Fig. 2).

TABLE VII.  
Hydrogenation Energies (kcal / mol) Classified According to Bond that Undergoes Hydrogenation and the Electronegativity of the Third Substituent of the Ring.

	H <sub>2</sub> C—CH <sub>2</sub>	H <sub>2</sub> C—NH	H <sub>2</sub> C—O	NH—NH	HN—O	O—O
CH <sub>2</sub>	36.6 (0 → 19)	40.1 (7 → 20)	40.9 (1 → 21)	55.6 (8 → 28)	69.7 (4 → 29)	91.1 (2 → 34)
NH	32.8 (7 → 22)	31.9 (8 → 23)	30.3 (4 → 24)	45.0 (9 → 30)	61.6 (6 → 31)	83.5 (5 → 35)
O	29.8 (1 → 25)	28.7 (4 → 26)	27.5 (2 → 27)	41.6 (6 → 32)	59.0 (5 → 33)	84.9 (3 → 36)

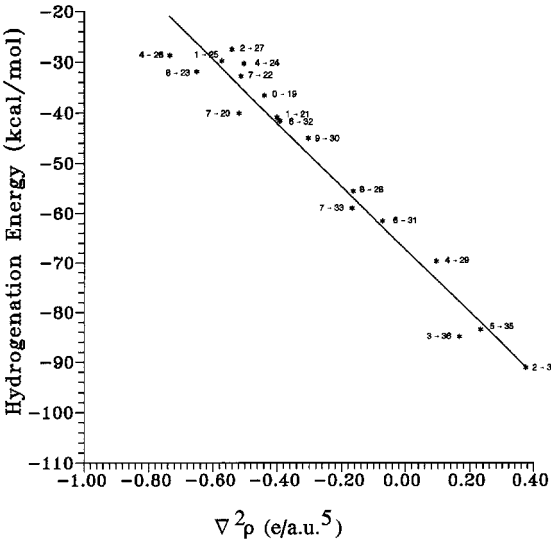


FIGURE 2. Correlation between G2 hydrogenation energies and the Laplacian of the charge density of the corresponding bcp.

As already discussed, there are two main factors governing the accumulation of charge in the bonds forming the ring: (a) the presence of —CH<sub>2</sub> groups, which can be polarized, adjacent to the bond; and (b) the influence of the third atom forming the ring, because the higher its electronegativity the greater the charge concentration on the bond between the other two atoms. The first factor explains why the bonds involving CH<sub>2</sub> groups (columns 1–3 of Table VII) have the lowest hydrogenation energies, whereas a large increment is observed if only —NH groups (columns 4 and 5 of Table VII) or —O groups (column 6 of Table VII) are present. The second factor is responsible for the large difference (13.4 kcal/mol) between the hydrogenation energy of oxirane (**1**) and dioxirane (**2**) and explains why the hydrogenation of the C—C bond of aziridine (**7**), or the N—N bond of oxadiaziridine (**6**) is less exothermic than similar processes in cyclopropane (**0**) or diaziridine (**8**), respectively.

These trends indicate the important role played by the hydrogen atoms in reinforcing the bonds of these systems. As pointed out by Wiberg et al.,<sup>42</sup> hydrogen atoms are easily depopulated, because the coulombic attractive potential felt by their electron distributions is the smallest of all atoms of the periodic system, hence they can donate charge easily when interacting with electron-withdrawing groups. This is actually the physical process that takes place in the hydrogenation reactions discussed earlier. A similar stabilizing mechanism was invoked by Wiberg et al.<sup>42</sup> for the particular case of carbanions and carbocations. This role of hydrogen atoms would also explain the trends in the ring strain energies of the TMRs.

### CONVENTIONAL RING STRAIN ENERGIES

Results in Table III show that, in agreement with previous findings,<sup>31,32,60</sup> the enthalpies of the isodesmic reactions do not yield useful information on the strain energies of the TMRs. Most of these isodesmic processes are thought to be endothermic or thermoneutral rather than exothermic as would be expected from the low stability of the cyclic species. In contrast, the CRSEs obtained using the corresponding homodesmotic reactions are in very good agreement with the available experimental values, the largest difference being 0.8 kcal/mol. In this respect, it is worth noting that the results change considerably with the level of theory employed. For instance, the CRSEs predicted for trioxirane using the homodesmotic reactions at the HF/6-31G\*, MP2/6-31G\*, and G2 levels are 38.8, 29.2, and 33.3 kcal/mol, respectively; the corresponding values for triaziridine are 31.9, 30.1, and 23.4 kcal/mol. The differences between HF and MP2 calculations show the dramatic effects of electron correlation, whereas the significant differences between the MP2 and G2 values indicate that high order correlation contributions, as well as more flexible basis sets, are required to adequately describe TMRs.

At this point, a question arises as to whether or not the CRSE would depend on the order of the homodesmotic reaction used, even at the G2 level. The use of  $s$ -homodesmotic reactions of order  $s \geq 2$  is impractical for the set of systems in which the atoms forming the ring are different, because the number of open structures required increases very rapidly with  $s$ . Thus, we have studied this problem initially for the cases in which the atoms forming the ring are the same (0,3,9). Even for these systems, calculations are rather expensive for

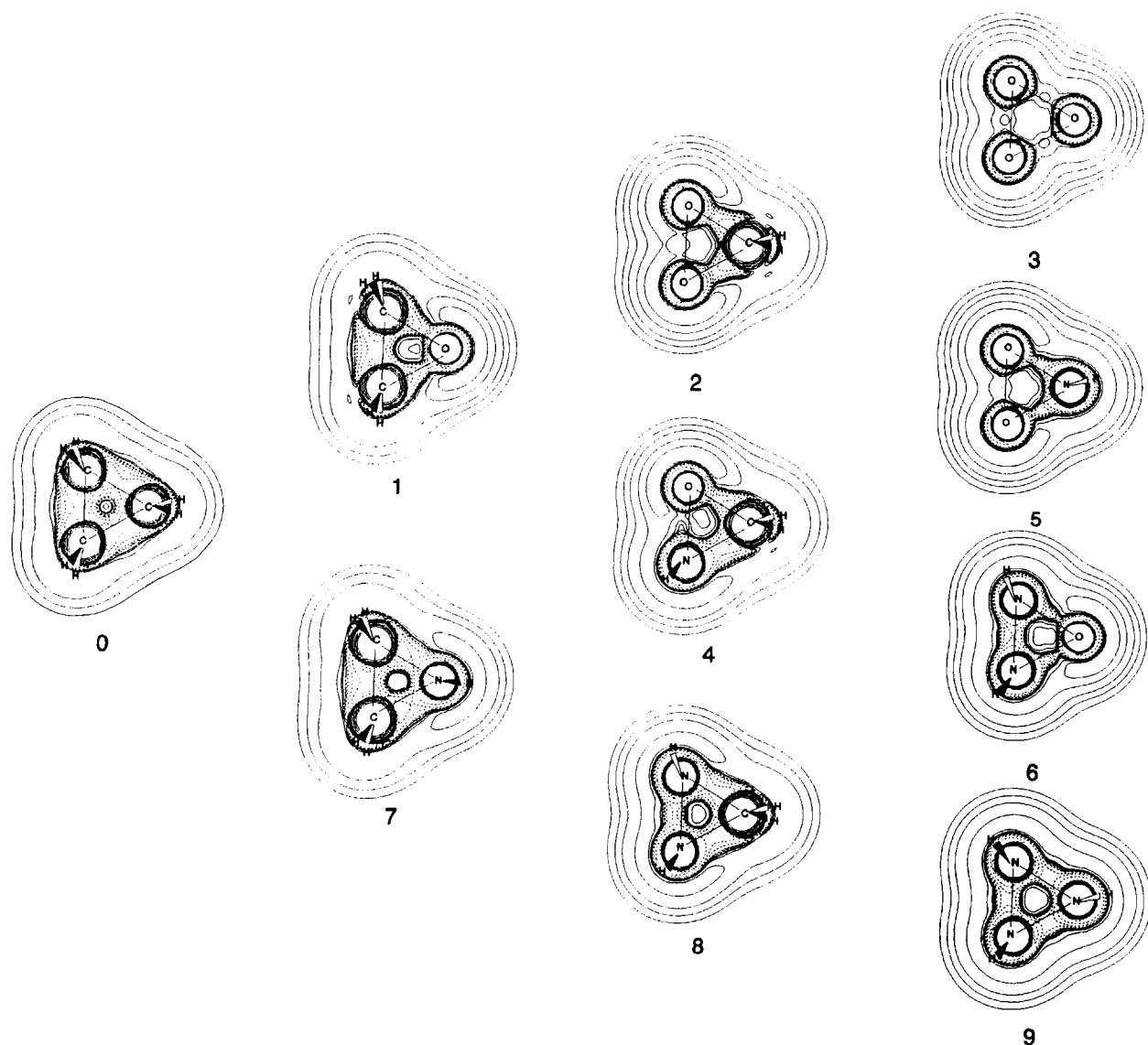
$s = 3$  and have been carried out at the G2(MP2) level for the sake of economy. The results obtained (see Table III) show a much greater stability when increasing  $s$  from 1 to 3 (33.3, 30.8, and 30.1 for trioxirane and 23.4, 24.8, and 26.2 for triaziridine) than the MP2/6-31G\* results of Zhao and Gimarc<sup>31,32</sup> (29.2, 23.0, and 23.8 for trioxirane and 30.1, 25.6, and 30.2 for triaziridine). It can also be seen that compounds **4** and **9** have rather small CSREs when estimated using  $s = 1$  homodesmotic reactions, whereas, in both cases, the CRSE increases if the order of the homodesmotic reaction increases. Even though the results at the G2 level are rather stable, it must be emphasized that the use of different values of  $s$  may yield differences of about 3 kcal/mol in the estimated CRSEs. Hence, this value should be taken as an upper limit of the accuracy of G2 CRSEs.

It is also important to realize that there is no strictly unbiased way of calculating ring strain energies within the set of TMRs considered in this study, because when the  $-\text{CH}_2$  groups in cyclopropane are replaced by  $-\text{NH}$  or  $-\text{O}$  other effects besides angular strain appear. For instance, in systems with two  $-\text{NH}$  groups as **6** and **8**, the amino hydrogens position at different sides of the ring plane to avoid repulsion. However, in triaziridine **9**, where three  $-\text{NH}$  groups are present, two amino hydrogens must necessarily be at the same side of the ring plane, affecting the stability of the system. Furthermore, because the open-chain reference compounds involved in the corresponding homodesmotic reactions are less rigid, they can adopt a conformation in which these repulsive interactions are minimized. In this respect, it is worth mentioning that, according to the G2 calculations of Schlegel et al.<sup>47</sup> on triazane (**30**), the energy gap between different conformers can be as large as 6 kcal/mol. Hence, the enthalpies of homodesmotic reactions involving these kinds of systems measure not only ring strain effects, but also nonbonding interactions, which are absent in systems such as dioxirane **2**, trioxirane **3**, etc. In the series of oxygen-containing compounds there is also an additional feature, related to the role of hydrogen atoms, which affects the calculated CRSE of trioxirane **3**. In the homodesmotic reactions involving **3** there is an important change in the environment of the oxygen atoms that does not take place for other systems. For instance, in the homodesmotic reactions involving cyclopropane **0**, the carbon atoms of the cyclic and the reference compounds are always bonded to hydrogen atoms, so the environment of the carbons does not differ

dramatically between both sides of the reaction. This is not the case for the homodesmotic reactions involving **3**, where only the reference systems have hydrogen atoms bonded to the oxygens.

The most conspicuous fact from Table III is that the ring strain in TMRs changes very little along the series. Nearly all TMRs considered have CRSEs around 26.5 kcal/mol, within a  $\pm 3.5$ -kcal/mol range. This is an unexpected finding if one considers<sup>34–36</sup> the CRSE as the result of two components: a destabilizing one due mainly to the angular strain and a stabilizing one due to the surface delocalization of electrons inside the ring (which

have been evaluated<sup>36</sup> to be of the order of 14–17 kcal/mol). Actually, in the light of these arguments, the almost constancy of the CRSEs of **0**, **1**, and **2**, should imply an increase of the surface delocalization of the charge density along the series. However, the capability of accumulating charge density inside the ring decreases as the  $-\text{CH}_2$  groups are replaced by oxygen atoms and, accordingly, the delocalization of charge should also be lower. The maps of the Laplacian of the charge density for all the TMRs included in this study (Fig. 3) clearly show that the accumulation of charge inside the cyclopropane ring (**0**) gradu-

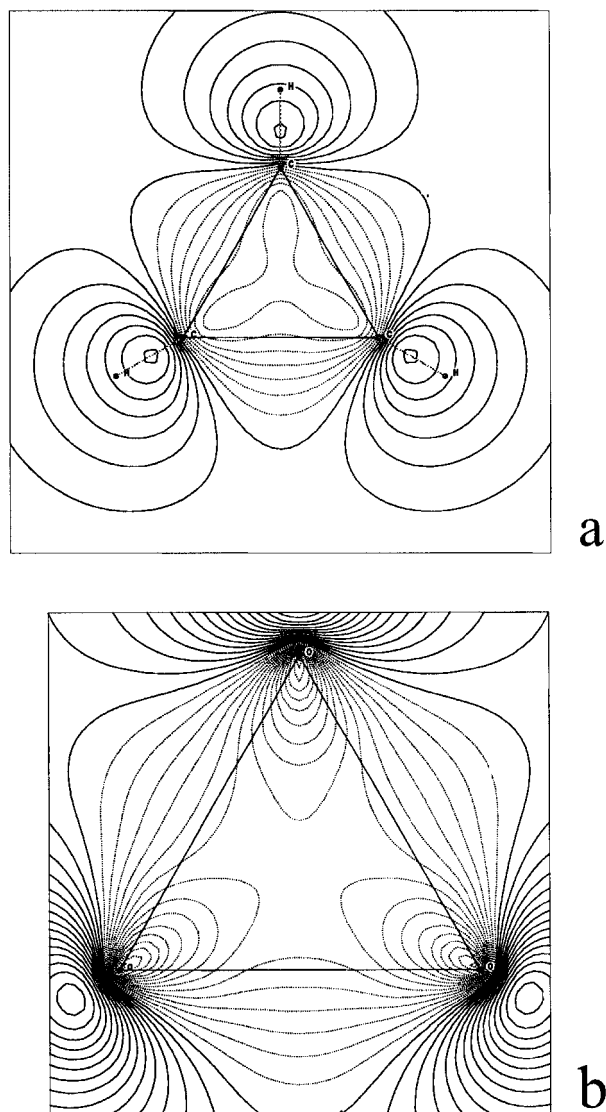


**FIGURE 3.** Contour maps of the Laplacian of the charge density for all TMRs considered in this study. Possible values of  $\nabla^2 \rho$  are denoted by solid lines and negative values by dashed lines. Contour values (in a.u.) are  $\pm 0.02$ ,  $\pm 0.04$ ,  $\pm 0.08$ ,  $\pm 0.2$ ,  $\pm 0.4$ ,  $\pm 0.8$ ,  $\pm 2$ ,  $\pm 4$ , and  $\pm 8$ .

ally decreases as the  $\text{CH}_2$  groups are systematically substituted by  $-\text{NH}$  or  $-\text{O}$ . As expected, the largest effect is observed for trioxirane **3**, where the electron charge density concentrates preferentially around and near the oxygen nuclei. The value of the Laplacian at the corresponding ring critical point (Table V) consistently and significantly increases along the 0, 1, 2, and 3, the 0, 7, 8, and 9, and the 7, 4, and 5 series of compounds. These findings are necessarily consistent with a molecular orbital description. As indicated in ref. 41, the so-called *surface orbital* ( $3a'_1$ ) of cyclopropane (see Fig. 4) is one of the MOs responsible for the concentration of charge at the ring center. An occupied MO with similar characteristics is found in trioxirane; however, because oxygen is much more electronegative than carbon, the corresponding  $p$  orbitals are less diffuse and they overlap less effectively inside the ring. The result is that the accumulation of charge at the center of the ring is disfavored with respect to its accumulation around the oxygen atoms. This picture is not in contradiction with that based on the spin-coupled theory where the stability of the C—C bonds in cyclopropane is explained<sup>39,40</sup> in terms of a geminal delocalization through the participation of each spin-coupled orbital in a bonding interaction over the other C—C bond involving the same methylene group. Furthermore, because the concentration of charge inside the ring depends strongly on the presence of groups with hydrogen atoms attached to the central atom, in particular  $-\text{CH}_2$  groups, it is not surprising to find a relatively good correlation between the Laplacian of the charge density at the ring critical point and the number of hydrogens of the ring (Fig. 5).

In summary, because surface delocalization of the electron density decreases when electronegative atoms are included, we must conclude that this effect cannot be the main contributor to the low CRSE calculated for systems other than cyclopropane.

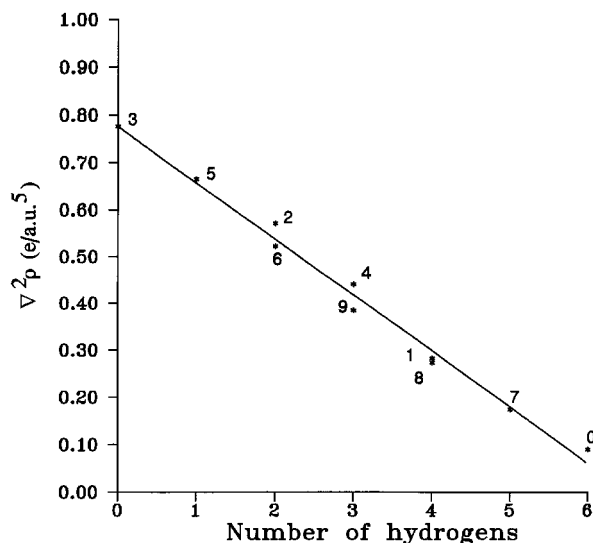
The predicted constancy of the CRSEs is in contrast with the conclusion of Kraka et al.<sup>25</sup> in the sense that the ring strain enthalpies for oxirane, dioxirane, and trioxirane show a constant increment of 5–6 kcal/mol. According to our results this finding was a consequence of using CRSEs not comparable in accuracy. Whereas the CRSE for dioxirane (32.8 kcal/mol) was based on CCSD(T)/TZ + 2P calculations,<sup>21</sup> the value taken for trioxirane (38.7 kcal/mol) was obtained at the HF/6-31G\* level.<sup>41</sup> We have already mentioned that, for this compound, the CRSE changes dramatically



**FIGURE 4.**  $3a'_1$  canonical molecular orbital of (a) cyclopropane and (b) trioxirane as obtained with a 6-31G\* basis set. Positive values of  $\rho$  are denoted by solid lines and negative values by dotted lines. The isodensity contour lines correspond, in both cases, to  $\pm 0.03$ ,  $\pm 0.06$ ,  $\pm 0.09$ .

when electron correlation effects are taken into account, so when all these systems are studied at the same (G2) level the aforementioned constant increment in the CRSEs is not observed.

There remains a significant difference between our calculated value for the CRSE of dioxirane and that reported in ref. 25. This disagreement arises from a sizeable difference in the estimated heat of formation of this compound. Whereas, CCSD(T)/TZ + 2P this value is 6.0 kcal/mol,<sup>21</sup> at the G2 level it is  $> 5.0$  kcal/mol lower. To check whether

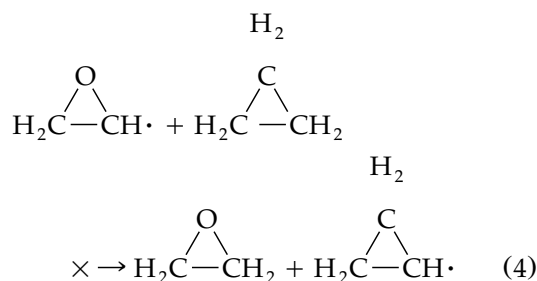


**FIGURE 5.** Correlation between the Laplacian of the charge density at the rcp and the number of hydrogens of the corresponding TMR.

this difference might be a consequence of the approximations inherent in G2 formalism, we have also estimated the heat of formation of dioxirane and trioxirane at the complete basis sets-atom pair natural orbital (CBS-APNO) level,<sup>22</sup> using QCISD/6-311G(d,p)-optimized geometries rather than MP2/6-31G\*-optimized ones. The values thus obtained (see Table III) differ from the G2 estimates by less than 1 kcal/mol, so we can conclude that similar trends in the CRSE would be obtained at the CBS-APNO level. In summary, we may safely conclude that our findings regarding the constancy of the CRSEs for nitrogen and oxygen containing three-membered rings would not change when more sophisticated theoretical models are employed.

This constancy of the CRSE is in agreement with the findings reported by Inagaki et al.,<sup>39</sup> and it is consistent with the explanation given by Wiberg et al.<sup>38</sup> and Schleyer<sup>13</sup> on the origin of the strain in TMR, in terms of the rehybridization of the C atoms of cyclopropane. The high *s* character of the hybrid orbitals results in an enhanced electronegativity of the carbon atoms, which can be satisfied by polarizing the electron charge away from the hydrogen atoms attached to them, leading to a stabilization of the C—C bonds. However, this occurs at the cost of destabilizing the CH bonds, which counterbalances the stabilizing effect of increasing the charge in the plane of the ring.

To confirm this from a more quantitative point of view we estimated the enthalpy of the following reaction:



which allows us to compare the relative strengths of the CH bonds in cyclopropane **0** and oxirane **1**. At the G2 level of theory, this reaction is predicted to be endothermic by 4.8 kcal/mol, which verifies that the CH bonds in oxirane are weaker than those in cyclopropane. This result is also consistent with the fact that the CH bond lengths increase as the number of electronegative groups within the ring increases (see Table VI). Concomitantly, non-negligible changes are also observed in the CH harmonic stretching frequencies; for instance, those of oxirane **1** appear 12 cm<sup>-1</sup> red-shifted, on average, with respect to those of cyclopropane **0**.

In the case of trioxirane there are no hydrogens to be polarized and no charge can be pulled into the ring. The Laplacian at the rcp is consistently quite positive, the O—O bonds are weak and long, and trioxirane is significantly less stable than its open isomer, ozone. However, the low stability of the O—O linkages of trioxirane is not reflected in a dramatic increase of its ring strain energy, because, although the aforementioned stabilizing effects are much smaller than in cyclopropane, the destabilizing contributions from the electron-depopulated CH bonds are absent.

In agreement with these arguments, while the experimental CRSE for cyclopropane is 25.1 kcal/mol, the value for the corresponding perfluorinated derivative ( $\approx 83.3$  kcal/mol)<sup>39</sup> is more than three times larger. As mentioned earlier, while the enhanced electronegativity of the carbon atoms of cyclopropane can be satisfied by depopulating the CH bonds, such a mechanism is not possible in perfluorocyclopropane due to the high electronegativity of the fluorine atoms and, accordingly, the CRSE increases dramatically.

Although the concentration of charge on the plane of the ring has small energetic consequences it has important chemical implications. We have already mentioned the effects on the strength of

the bonds, on the hydrogenation energies and on the acidic character of the  $\text{—CH}_2$  and  $\text{—NH}$  hydrogens. But there are also remarkable effects as far as the reactivity of these systems is concerned. Consider, for instance, the  $\text{Li}^+$ -association processes. For cyclopropane, the most stable complex corresponds to the attachment of the metal monocation to the  $\text{H}_2\text{C—CH}_2$  bond in the plane of the ring,<sup>23</sup> which is strongly favored by the concentration of charge in that plane. In contrast, the interaction of  $\text{Li}^+$  with trioxirane does not show any minimum with the  $\text{Li}^+$  lying in the plane of the ring, and the only stable form corresponds to a complex in which  $\text{Li}^+$  is over the plane of the ring.<sup>62</sup>

## Conclusions

In ABX three-membered rings the decrease in the A—B bond length as the electronegativity of X increases is significantly larger than that found for the corresponding acyclic analogs. In general, a systematic substitution of the  $\text{—CH}_2$  groups of cyclopropane **0** by  $\text{—NH}$  or  $\text{—O}$  groups implies significant geometrical changes that are not reflected in a parallel change of the corresponding CRSEs, which are nearly constant upon substitution. In the light of our analysis, we conclude that the significant charge redistribution caused by an electronegative group within the ring is dumped by the remaining  $\text{CH}_2$  groups attached to them. The role of these groups is to supply the charge density that has been depleted by the electronegative substituent, maintaining the stability of the linkages of the ring. This involves an energy cost, because the CH bonds themselves become destabilized. Accordingly, the system that presents the highest CRSE is trioxirane, where no hydrogens exist. However, even in this case, the CRSE is not dramatically high, because, although no charge can be moved into the bonding regions, the destabilizing effects associated with the depopulated CH bonds are also absent. At this point it is worth mentioning that, according to the very recent work of Johnson and Borden,<sup>27</sup> the changes in the strain of methylenecyclopropane and 1-methylcyclopropene with respect to cyclopropane are essentially due to the loss of a very strong cyclopropane CH bond. A similar stabilizing role of the hydrogen atoms has also been discussed very recently by Wiberg et al.<sup>45</sup> for the particular case of carbocations and carbanions. The fact that the charge

delocalization clearly decreases when  $\text{—CH}_2$  groups are replaced by  $\text{—NH}$  or  $\text{—O}$  groups, while the CRSEs remain almost constant, seems to rule out  $\sigma$ -aromaticity as a dominant stabilizing factor along the series of TMRs. Although CRSEs vary only very slightly, significant changes in the hydrogenation energies of the TMRs investigated have been found. When in an ABC three-membered ring the electronegativity of C increases, the hydrogenation energy of the A—B bond decreases and vice versa. In general, there is good linear correlation between calculated hydrogenation energies and the Laplacian at the bcp of the linkage involved in the hydrogenation processes.

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